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IX.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF
HARVARD COLLEGE.

ON MUCOPHENOXYBROMIC ACID.

BY HENRY B. HILL AND EDWARD K. STEVENS.

Presented May 29, 1883.

THE products which are formed when mucobromic acid is treated with a large excess of baric hydrate, have already been described by O. R. Jackson and one of us.* Formic and dibromacrylic acids were found to be the first products of this reaction, although even in the cold a part of the dibromacrylic acid was further converted into bromopropiolic acid. Later experiments undertaken with the view of avoiding this secondary decomposition, showed that an entirely different reaction ensued when the conditions were so modified that the solution was at no time strongly alkaline.† The chief product formed in this case was easily found to be an acid containing four atoms of carbon and one of bromine; but the determination of its constitution proved to be a matter of more difficulty, and a description of it must therefore be postponed until it can be further studied. Since it seemed possible that sodic ethylate or potassic phenylate might react upon mucobromic acid and yield similar products, whose constitution could more easily be determined, we turned our attention in this direction. Although we have been unable to obtain any such products by the action of sodic ethylate, potassic phenylate has given us well-defined products containing the phenoxyl group.

Mucophenoxybromic Acid.

Potassic phenylate acts upon potassic mucobromate in aqueous solution at ordinary temperatures; but the isolation of the potassic mucophenoxybromate thus formed is somewhat difficult, and we have

* These Proceedings, Vol. XVI. (N. S. VIII.) p. 188.† *Loc. cit.*, p. 204.

not been able to obtain uniform results in our various preparations. We have found it advantageous to use a large excess of potassic phenylate, and to add also potassic hydrate in quantity sufficient to neutralize the mucobromic acid taken. We usually have dissolved 25 grms. of crystallized phenol and 17.5 grms. of ordinary potassic hydrate in 30 grms. of water, and after the solution is well cooled, have added 20 grms. of mucobromic acid. After the lapse of a short time small compact rhombic crystals of the new potassium salt begin to separate, and the reaction is ordinarily completed in less than an hour. The crystals should then be collected at once, drained by the pump, and washed with a little cold water. Hydrochloric acid added to an aqueous solution of the salt then precipitates mucophenoxybromic acid in clustered needles, which, when dried over sulphuric acid, gave the following results:—

- I. 0.2156 grm. substance gave on combustion 0.3486 grm. CO_2
and 0.0525 grm. H_2O .
II. 0.2250 grm. substance gave 0.1564 grm. AgBr .
III. 0.2168 grm. substance gave 0.1504 grm. AgBr .

	Calculated for $\text{C}_4\text{H}_2(\text{OC}_6\text{H}_5)\text{BrO}_3$.	I.	Found. II.	III.
C	44.28	44.11		
H	2.58	2.71		
Br	29.52		29.58	29.52

When crystallized from hot water, mucophenoxybromic acid forms small flat prisms concentrically grouped, which melt at $104-105^\circ$. The acid is readily soluble in hot water, sparingly in cold; readily soluble in alcohol or ether, soluble in hot benzol or chloroform, and almost insoluble in carbonic disulphide or ligroin. An aqueous solution of the acid reduces silver oxide on warming, and gives with ferric chloride a whitish precipitate.

Potassic Mucophenoxybromate. $\text{KC}_4\text{H}(\text{OC}_6\text{H}_5)\text{BrO}_3$. The salt obtained by the action of potassic phenylate upon mucobromic acid was recrystallized several times from warm water. It formed then oblique tabular crystals quite soluble even in cold water. The salt is more stable in aqueous solution than the corresponding mucobromate, and yet suffers quite rapid decomposition at temperatures near 100° . The salt dried by exposure to the air contains no water of crystallization.

- I. 0.4314 grm. of the salt gave on ignition with H_2SO_4 0.1227 grm. K_2SO_4 .

II. 0.4430 grm. of the salt gave on ignition with H_2SO_4 0.1255 grm. K_2SO_4 .

	Calculated for	Found.	
	$\text{KC}_4\text{H}(\text{OC}_6\text{H}_5)\text{BrO}_3$.	I.	II.
K	12.65	12.76	12.72

Baric Mucophenoxybromate. $\text{Ba}(\text{C}_4\text{H}(\text{OC}_6\text{H}_5)\text{BrO}_3)_2 \cdot 3\text{H}_2\text{O}$. This salt was obtained by neutralizing a cold aqueous solution of the acid with baric carbonate, and allowing the solution thus obtained to evaporate spontaneously. It separated in leafy rhombic crystals, which were very soluble in water. On warming the solution decomposition ensued. The air-dried salt contained three molecules of water, one of which it lost over sulphuric acid, the rest at 100° .

I. 0.8147 grm. of the air-dried salt lost over H_2SO_4 0.0213 grm. H_2O , and in addition 0.0403 grm. at 100° .

II. 0.7863 grm. of the air-dried salt lost over H_2SO_4 0.0201 grm. H_2O , and in addition 0.0397 grm. at 100° .

	Calculated for	Found.	
	$\text{Ba}(\text{C}_4\text{H}(\text{OC}_6\text{H}_5)\text{BrO}_3)_2 \cdot 3\text{H}_2\text{O}$.	I.	II.
H_2O	2.46	2.61	2.56
3 H_2O	7.39	7.56	7.61

0.4628 grm. of the salt dried at 100° gave on ignition with H_2SO_4 0.1599 grm. BaSO_4 .

	Calculated for	Found.
	$\text{Ba}(\text{C}_4\text{H}(\text{OC}_6\text{H}_5)\text{BrO}_3)_2$.	
Ba	20.23	20.32

When treated with an excess of an alkaline hydrate, mucophenoxybromic acid, like mucobromic, is decomposed, and yields a substituted acrylic acid together with formic acid.

Phenoxybromacrylic Acid.

We have found it most convenient to dissolve equal weights of potassic hydrate and potassic mucophenoxybromate each in their own weight of water, and to mix the hot solutions. On cooling, potassic phenoxybromacrylate separates in well-formed crystals. From these, by the addition of hydrochloric acid, we prepared the acid which, when recrystallized from hot water and dried over sulphuric acid, gave the following results:—

I. 0.2037 grm. of the substance gave on combustion 0.3307 grm. CO_2 and 0.0553 grm. H_2O .

- II. 0.2027 grm. of the substance gave 0.1577 grm. AgBr.
 III. 0.2238 grm. of the substance gave 0.1739 grm. AgBr.

	Calculated for $C_3H_2(OC_6H_5)BrO_2$.	I.	Found. II.	III.
C	44.44	44.27		
H	2.88	3.02		
Br	32.93		33.11	33.07

Phenoxybromacrylic acid crystallizes from hot water in long silky needles, which melt at 138° . It is almost insoluble in cold water, and is somewhat sparingly soluble even in boiling water. In ether or alcohol it is very soluble; in chloroform or benzol it dissolves on warming, and crystallizes as these solutions cool. Carbonic disulphide dissolves it with more difficulty.

Potassic Phenoxybromacrylate. $KC_3H(OC_6H_5)BrO_2$. On cooling the hot solution of potassic mucophenoxybromate in potassic hydrate, potassic phenoxybromacrylate separates in well-formed rhombic plates, which may be recrystallized from hot water, although they are quite soluble even in cold water. The air-dried salt proved to be anhydrous.

- I. 0.5073 grm. of the air-dried salt gave on ignition with H_2SO_4
 0.1588 grm. K_2SO_4 .
 II. 0.5077 grm. of the air-dried salt gave on ignition with H_2SO_4
 0.1572 grm. K_2SO_4 .

	Calculated for $KC_3H(OC_6H_5)BrO_2$.	I.	Found. II.
K	13.91	14.06	13.90

Baric Phenoxybromacrylate. $Ba(C_3H(OC_6H_5)BrO_2)_2 \cdot 5H_2O$. On neutralizing a boiling solution of the acid with baric carbonate, and evaporating on the water-bath, the barium salt was obtained in the form of radiating prisms, which were permanent in the air and hardly lost in weight over sulphuric acid. It was freely soluble in cold water. The air-dried salt gave on analysis:—

- I. 1.2120 grm. of the air-dried salt lost at 110° 0.1535 grm. H_2O .
 II. 1.0468 grm. of the air-dried salt lost at 110° 0.1345 grm. H_2O .
 III. 0.6687 grm. of the air-dried salt lost at 110° 0.0855 grm. H_2O .

	Calculated for $Ba(C_3H(OC_6H_5)BrO_2)_2 \cdot 5H_2O$.	I.	Found. II.	III.
H_2O	12.66	12.67	12.85	12.78

0.5017 grm. of the salt dried at 110° gave on ignition with H_2SO_4 0.1873 grm. BaSO_4 .

	Calculated for $\text{Ba}(\text{C}_3\text{H}(\text{OC}_6\text{H}_5)\text{BrO}_2)_2$.	Found.
Ba	22.06	21.95

Calcic Phenoxybromacrylate. $\text{Ca}(\text{C}_3\text{H}(\text{OC}_6\text{H}_5)\text{BrO}_2)_2 \cdot 5\text{H}_2\text{O}$. The calcium salt was prepared from the acid by neutralizing its aqueous solution with calcic carbonate. It was readily soluble in water, and crystallized on cooling its concentrated solution in clustered needles, which were permanent in the air or over sulphuric acid.

I. 0.9361 grm. of the air-dried salt lost at $100-105^{\circ}$ 0.1381 grm. H_2O .

II. 0.7563 grm. of the air-dried salt lost at $100-105^{\circ}$ 0.1122 grm. H_2O .

	Calculated for $\text{Ca}(\text{C}_3\text{H}(\text{OC}_6\text{H}_5)\text{BrO}_2)_2 \cdot 5\text{H}_2\text{O}$.	Found.	
		I.	II.
H_2O	14.66	14.75	14.84

0.5046 grm. of the salt dried at $100-105^{\circ}$ gave on ignition with H_2SO_4 0.1310 gr. CaSO_4 .

	Calculated for $\text{Ca}(\text{C}_3\text{H}(\text{OC}_6\text{H}_5)\text{BrO}_2)_2$.	Found.
Ca	7.64	7.64

Argentio Phenoxybromacrylate. $\text{AgC}_3\text{H}(\text{OC}_6\text{H}_5)\text{BrO}_2$. The silver salt may be precipitated by the addition of argentic nitrate to a hot aqueous solution of the acid. It crystallizes in needles which may be recrystallized without decomposition from boiling water. When dried over sulphuric acid, the salt gave the following results:—

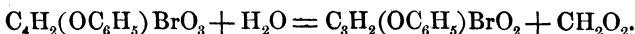
I. 0.4464 grm. of the salt gave on precipitation with HBr 0.2391 grm. AgBr .

II. 0.4240 grm. of the salt gave on precipitation with HBr 0.2268 grm. AgBr .

	Calculated for $\text{AgC}_3\text{H}(\text{OC}_6\text{H}_5)\text{BrO}_2$.	Found.	
		I.	II.
Ag	30.85	30.77	30.72

Phenoxybromacrylic acid is therefore one of the products formed from mucophenoxybromic acid by the action of potassic hydrate. The mother liquors from which the potassic phenoxybromacrylate had crystallized yielded on acidification with dilute sulphuric acid and distillation an acid distillate, which gave with ferric chloride and bromine water reactions showing the presence of small quantities of phenol. When neutralized with calcic carbonate and evaporated, it left calcic

formiate, which was identified by its characteristic behavior with argentic nitrate and mercuric chloride. The decomposition of mucophenoxybromic acid by potassic hydrate may therefore be expressed by the reaction : —



While dibromacrylic acid passes readily into brompropionic and malonic acids in an alkaline solution, phenoxybromacrylic acid is apparently unaltered by aqueous potassic hydrate. Even after long boiling in a concentrated solution (2 : 1) no potassic bromide is formed.

Phenoxybrommaleic Acid.

On warming a solution of mucophenoxybromic acid with argentic oxide, metallic silver is readily formed. If the solution is then heated to boiling, and the silver precipitated by hydrochloric acid, the filtered solution deposits on cooling phenoxybrommaleic acid in the form of fine felted needles. Their melting-point, when taken in the ordinary way, we found to be 103–104°; but when slowly heated, the melting-point was materially lowered, probably through the formation of the anhydride. From the analysis of substance which had been dried over sulphuric acid, it would seem that here also a certain amount of the anhydride was formed, and that in this respect its behavior is perfectly analogous to that of dibrommaleic acid which is partially converted into anhydride by drying, as one of us has shown : * —

- I. 0.1213 grm. of substance dried over H_2SO_4 gave on combustion 0.1935 grm. CO_2 and 0.0245 grm. H_2O .
 II. 0.2204 grm. of substance dried over H_2SO_4 gave 0.1494 grm. AgBr .

	Calculated for $\text{C}_4\text{H}_2(\text{OC}_6\text{H}_5)\text{BrO}_4$.	Calculated for $\text{C}_4(\text{O}_2\text{C}_6\text{H}_5)\text{BrO}_3$.	Found.	
			I.	II.
C	41.81	44.61	43.51	
H	2.44	1.86	2.25	
Br	27.87	29.74		28.85

Ratio of carbon to bromine atoms as found = 10 : 0.995.

Argentic Phenoxybrommaleate. $\text{Ag}_2\text{C}_4(\text{OC}_6\text{H}_5)\text{BrO}_4$. By the addition of argentic nitrate to an aqueous solution of the acid, the silver salt is precipitated in the form of clustered rhombic plates, which may

* These Proceedings, Vol. XVI. (N. S. VIII.) p. 178.

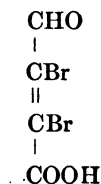
be recrystallized from boiling water without decomposition. The dry salt is decomposed suddenly by heat, but without detonation.

- I. 0.3922 grm. of the salt dried over H_2SO_4 gave on precipitation with HBr 0.2928 grm. AgBr .
 II. 0.2903 grm. of the salt dried over H_2SO_4 gave on precipitation with HBr 0.2168 grm. AgBr .

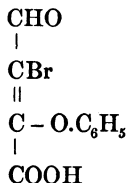
Ag	Calculated for	Found.	
	$\text{Ag}_2\text{C}_4(\text{OC}_6\text{H}_5)\text{BrO}_4$.	I.	II.
	43.12	42.88	42.90

The relation which mucophenoxybromic acid bears to mucobromic is sufficiently shown by its conversion into phenoxybromacrylic and phenoxybrommaleic acids under conditions identical with those necessary to the formation of dibromacrylic and dibrommaleic acids from mucobromic. Furthermore, it is evident that the extreme stability of the phenoxybromacrylic acid in alkaline solution shows that the phenoxyl group has taken the place of the bromine atom which is so readily removed from the corresponding dibromacrylic acid in the formation of brompropionic acid.

If mucobromic acid be written,



it follows that mucophenoxybromic acid has the form, —



and the acrylic acid derived from it has the form, —

